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Deactivation by Coking of Rhodium Catalysts of Widely Varying Dispersion

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The deactivation occurring in the course of cyclopentane conversion over Rh/Al_2O_3 has been investigated. The decay of catalytic activity can be represented by the theoretical models proposed in the literature. The deactivation rate constant determined from this model varies when the percentage of exposed Rh changes. Deactivation on rhodium therefore belongs to the class of structure-sensitive reactions. The different behaviors of Pd/Al_2O_3 and Rh/Al_2O_3 catalysts are discussed.

INTRODUCTION

The quantitative description of catalyst coking is of major importance both for industrial practice and for laboratory determinations of catalytic activities. Mathematical models have been proposed to represent catalyst fouling (*1–3*) and coke profiles in the catalytic bed (*4, 5*). In a recent review Froment (*6*) emphasized that the mathematical solutions are complex in the general case and it must be realized that simple expressions will be obtained only in limiting cases, where the reaction follows a simple kinetic law. The hydrogenolysis of cyclopentane may be one of these reactions, since it proceeds at the metallic surface at low temperatures and follows a zero order relative to the hydrocarbon on Pd and Rh. In the case of Pd/Al_2O_3 (*7*), the decay of catalytic activity as a function of time could be analyzed using a simple kinetic model proposed by Levenspiel *et al.* (*1–3*). The deactivation rate constant k_d was found to be independent of the dispersion of palladium, like the turnover for hydrogenolysis. However, sulphur repressed selectively hydrogenolysis and self-poisoning, whereas iron, which inhibits hydrogenation, left deactivation and hydrogenolysis unaffected. (*8*). These results suggest a structure sensitivity for deactivation. In the case of Rh/Al_2O_3 a particle size effect appears in the hydrogenolysis of cyclopentane (*9*), and it was therefore interesting to investigate the behaviour of deactivation. This was the objective of the present work.

EXPERIMENTAL

Catalysts. The preparation and characterization of the catalyst samples used in this work have been described in detail previously (*9*).

Apparatus and procedure. Cyclopentane for spectroscopy (purity = 99.7%) from Fluka was used as a reactant without further purification.

A continuous flow microreactor was used at low conversion, to minimize heat and mass transfer limitations. Catalytic properties were determined on an aliquot of the sample used for dispersion measurements. The sample was reactivated in flowing H_2 for 2 hr at 400°C. The reaction was performed at 225°C using a partial pressure of hydrocarbon of 100 Torr and a partial pressure of hydrogen of 660 Torr. The conversion was measured for several hours at

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intervals of 15 min. On-stream gas chromatography was used for analysis. The products of hydrogenolysis are paraffins ranging from methane to *n*-pentane.

The importance of diffusional limitations was estimated by applying the criterion of Weisz (*10*) to the experimental results. The highest rate of reaction was $6 \cdot 10^{-5}$ mole/sec/g when using a partial pressure of cyclopentane of 100 Torr and grain sizes in the 10^{-2}-cm range. The effective diffusivity D_{eff} may be estimated to be 10^{-3} cm²/sec for this type of catalyst. Taking $\rho = 0.6$ cm³/g for the density we obtain

$$\Phi = \frac{R^2 \rho}{D_{\mathrm{eff}} C_{\mathrm{A}}} \left(- \frac{dn_{\mathrm{A}}}{dt} \right) \simeq 0.6,$$

$\Phi < 1$ ensures an effectiveness factor close to unity. However, it appears also that diffusional limitations may be expected at higher temperatures.

RESULTS AND DISCUSSION

Kinetics of Deactivation

The activity decays as a function of time according to the hyperbolic law proposed by Germain and Maurel (*11*). The kinetic model previously used (*7*) was applied in the present case, with the same assumptions, namely, separability of the rate and deactivation laws, and similarity of the differential reactor to a well-mixed reactor.

Following Levenspiel (*2*) the deactivation law may be written as follows for the case of a zero order for hydrogenolysis:

$$\frac{W}{F_{\mathrm{A}_0}} = \frac{C_{\mathrm{A}_0} - C_{\mathrm{A}}}{kC_{\mathrm{A}_0}} + \frac{C_{\mathrm{A}_0} - C_{\mathrm{A}}}{kC_{\mathrm{A}_0}} k_{\mathrm{d}}(C_{\mathrm{A}})^p t,$$

where,

W is the mass of the catalyst sample,
F_{A_0} the feed rate of reactant A,
C_{A} the partial pressure of the reactant after reaction,
C_{A_0} the partial pressure of A fed to the reactor,
k the rate constant of hydrogenolysis,
k_{d} the rate constant of deactivation,
p the order relative to A for deactivation.

The slope of the reverse conversion as a function of time is then a straight line, the slope of which $k_{\mathrm{e}} = (k_{\mathrm{d}}(C_{\mathrm{A}_0})^p/k)\,(F_{\mathrm{A}_0}/W)$ allows the determination of rate constant k_{d}. Since the determination of k_{d} is based on the reliability of the model, it was of importance to check its applicability in the present case, and this was the aim of the kinetic study.

The influence of the weight of the sample is illustrated in Table 1, which shows that the amount of catalyst does not influence the value of k_{d} when W/F_{A_0} is kept constant. The influence of the partial pressure of cyclopentane is shown in Table 2: k_{e} increases with the partial pressure, while the initial activity remains constant. The order relative to cyclopentane is therefore zero for hydrogenolysis and close to 2 for deactivation.

TABLE 1

Influence of the Sample Weight and Flow of Reactant on Deactivation for Rh/Al$_2$O$_3$ Catalysts; Temperature 225°C

Weight (mg)	Flow (ml · sec)	Initial activity (10^6 mole/sec · g)	k_{e} (10^4 min^{-1})	$k_{\mathrm{d}} \simeq k_{\mathrm{e}} \times k$
200	2	6.2	9	5.58
100	1	5.2	8	4.16
50	0.5	5.2	9	4.68
25	0.25	4.0	11	4.4

TABLE 2

Influence of the Partial Pressure of cyclopentane on the Slope of the Deactivation Plot and Initial Activity for Rh/Al_2O_3 Catalysts; Temperature 225°C, Weight of Samples 50 mg

Partial pressure (Torr)	Concentration of reactant (mole/liter)	$k_e \cdot 10^4$ min^{-1}	Initial activity (10^6 mole/sec · g)
35.2	0.0021	3.1	9.5
47.0	0.0029	6.9	11.1
59.0	0.0036	10.3	10.6
76.7	0.0047	13.4	10
104	0.0064	22	11.9
164	0.0101	27	8.9

The influence of temperature on deactivation is similar to that previously found for Pd/Al_2O_3 (*7*):

(a) At the lower temperatures, where diffusional limitations do not perturb, the plot of log k_e as a function of reciprocal temperature obeys an Arrhenius law, with an apparent activation energy of 10 kcal/mole. Since k_d and k are rate constants, that finding may be considered a good test of the internal consistency of the results. The true activation energy for self-poisoning can then be estimated from the activation energy for hydrogenolysis (24 kcal/mole) to be 34 kcal/mole. For Pd/Al_2O_3 the activation energies were 40 kcal/mole for hydrogenolysis and 63 kcal/mole for deactivation (*7*). The lower values obtained for rhodium reflect the higher activity of that metal in both reactions.

(b) At higher temperatures, the deactivation law shifts to the third-order law predicted by the model (*3*) when pore diffusion resistance is implied.

The kinetic model may then be applied on rhodium also.

Influence of the Dispersion of Rhodium

The main objective was to determine if self-poisoning is structure sensitive or insensitive. The influence of the dispersion of rhodium is summarized in Fig. 1, which shows that deactivation changes significantly with dispersion in the case of Rh/Al_2O_3. The maximum change of k_d is by a factor of 4 to 5, which is beyond experimental error.

Self-poisoning therefore belongs to the class of structure-sensitive reactions, at least on rhodium. It must be pointed out that hydrogenolysis was also found to be structure sensitive on these catalysts (*9*).

By comparing Figs. 1 and 2, we observe that the patterns for deactivation and hydrogenolysis are different. A better correlation is obtained between deactivation and

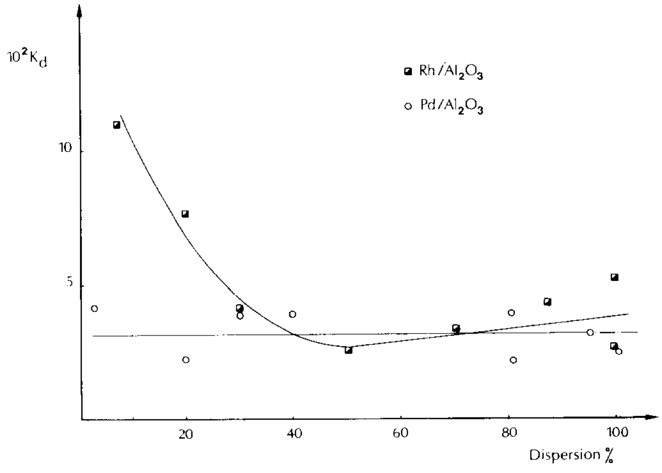

FIG. 1. Influence of the dispersion of the metallic phase on the deactivation rate constant for Rh/Al_2O_3 at 225°C and for Pd/Al_2O_3 at 290°C (Ref. (*7*)).

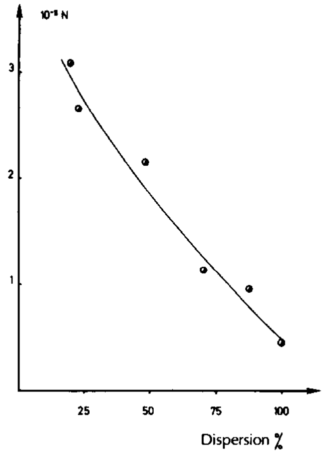

FIG. 2. Activity for cyclopentane hydrogenolysis on Rh/Al_2O_3. N is expressed in molecules converted per hour and per surface rhodium atom.

the selectivity for methane production previously reported (*9*). Deep hydrogenolysis and coke formation could proceed through the same highly dehydrogenated species proposed by Paál *et al.* (*12*).

Other authors (*13*) have assumed a common intermediate for hydrogenolysis and coking. However, the steady-state approximation applied to self-poisoning, assuming a common intermediate for hydrogenolysis and coke formation, gives the same influence of the pressure of hydrocarbon on the two reactions. For Pd/Al_2O_3 and Rh/Al_2O_3 hydrogenolysis of cyclopentane is found to follow a zero order, whereas self-poisoning follows a second order. This observation can hardly be reconciled with the assumption of a common intermediate and suggests different paths for the two reactions.

Self-poisoning appears as a structure-sensitive reaction on rhodium and should therefore be sensitive to alloying or selective poisoning (*14*).

Rhodium behaves quite differently from palladium, on which no influence of the dispersion could be detected on hydrogenolysis or self-poisoning. Moreover, facetted Pd/MgO catalysts give the same turnover number for hydrogenolysis as Pd/Al_2O_3 samples (*15*).

However, the existence of a selective poisoning by sulphur demonstrates that self-poisoning proceeds at specific surface sites in the case of palladium also, and therefore demonstrates structure sensitivity. The lack of influence of the size of palladium particles could then be interpreted by a reconstruction of the surface, probably by hydrogen.

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